Supporting Information

High thermoelectric power factor of poly(3-hexylthiophene) through in-plane alignment and doping with a molybdenum dithiolene complex

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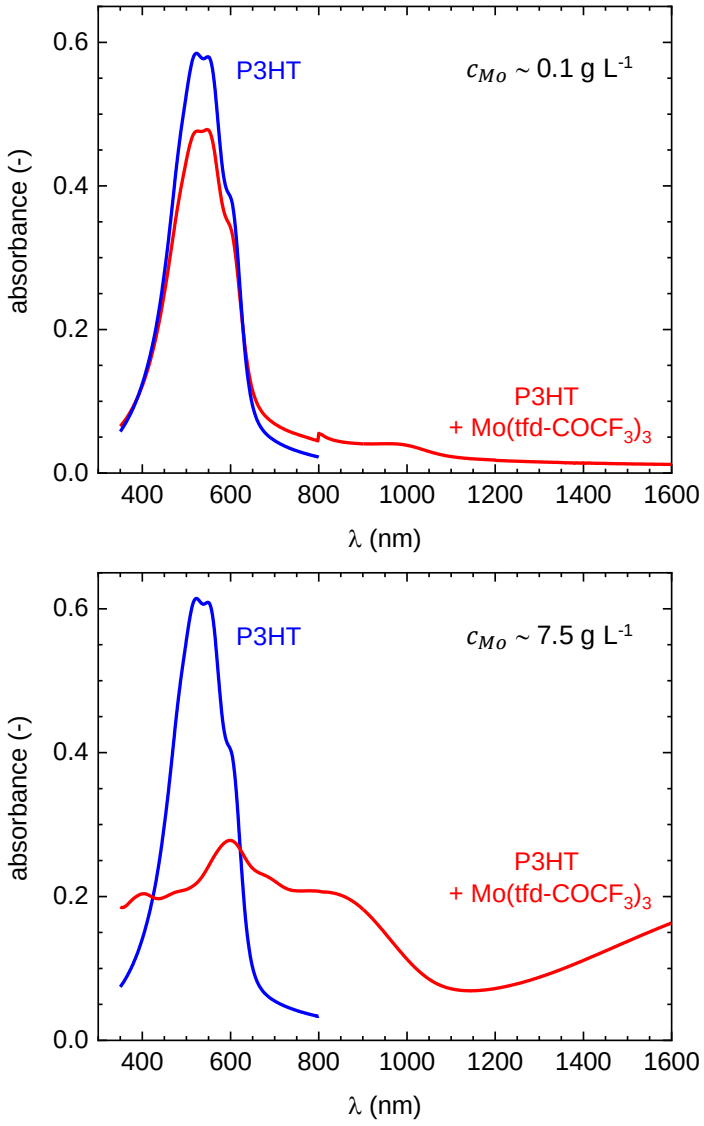

Figure S1. UV-vis-NIR absorbance spectra of a P3HT film before (blue) and after (red) sequential doping with Mo(tfd-COCF$_3$)$_3$: c_{Mo} ~ 0.1 g L^{-1} (top), c_{Mo} ~ 7.5 g L^{-1} (bottom).

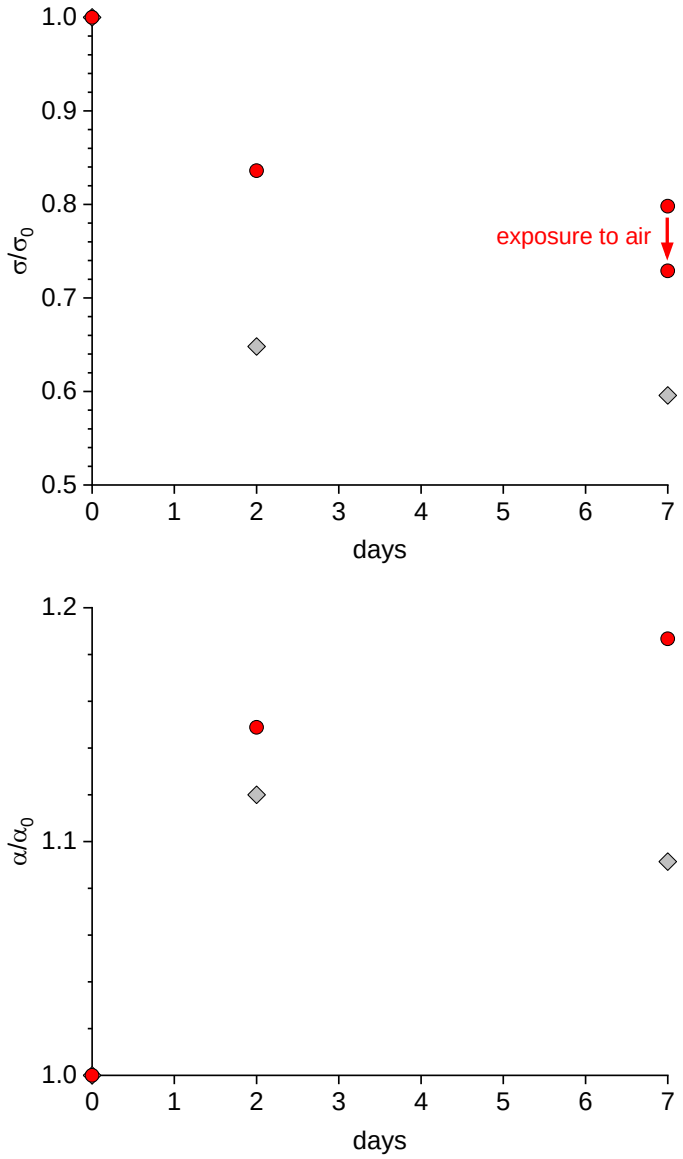

Figure S2. Change in conductivity σ/σ_0 (top) and Seebeck coefficient α/α_0 (bottom) of P3HT doped with c_{Mo} ~ 7.5 g L^{-1} during storage in a glove box; gray diamonds: neat P3HT (σ_0 ~ 285 S cm^{-1}; α_0 ~ 35 µV K^{-1}); red circles: rubbed P3HT parallel to rubbing direction (σ_0 ~ 681 S cm^{-1}; α_0 ~ 43 µV K^{-1}); after 7 days storage in a glove box the rubbed samples was exposed to air.

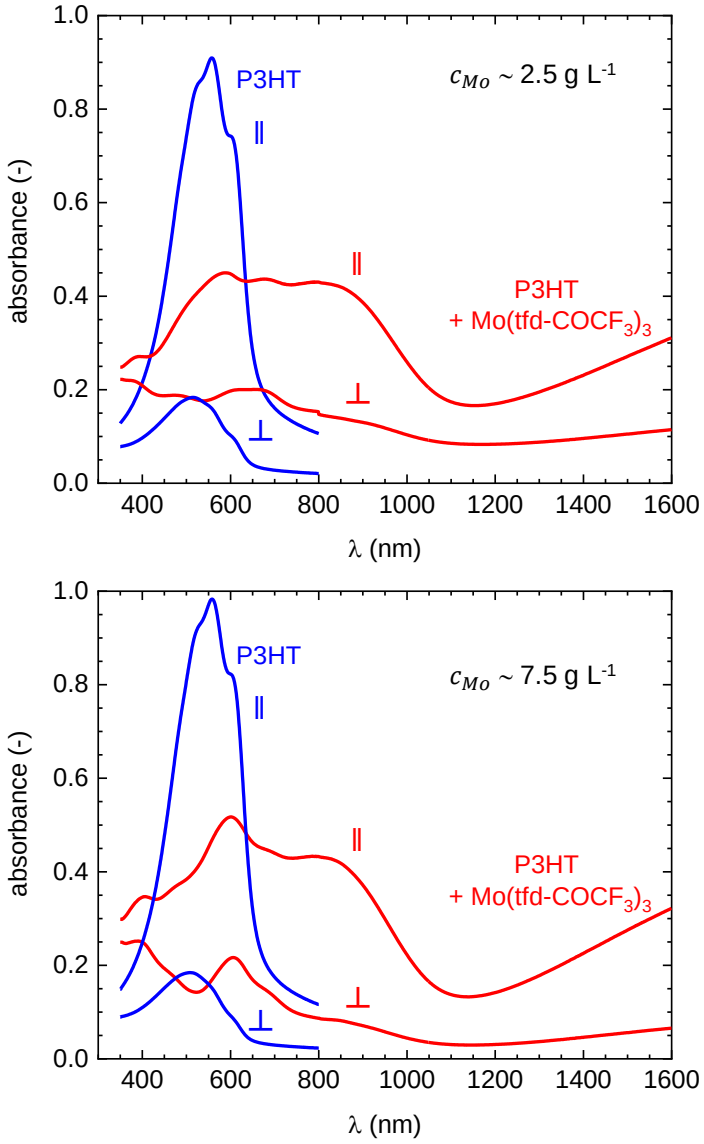

Figure S3. Polarized UV-vis-NIR absorbance spectra of rubbed P3HT and the same P3HT film sequentially doped with Mo(tfd-COCF$_3$)$_3$, c_{Mo} ~ 2.5 g L^{-1} (top) and c_{Mo} ~ 7.5 g L^{-1} (bottom), measured parallel (∥) and perpendicular (⊥) to the rubbing direction R.

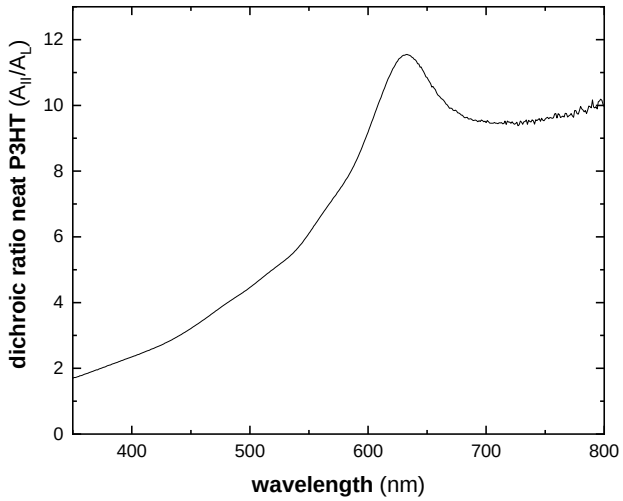

Figure S4. Dichroic ratio of neat rubbed P3HT versus wavelength; at 633 nm a maximum dichroic ratio of $A_{\parallel}/A_{\perp}$ ~ 11.5 is obtained.

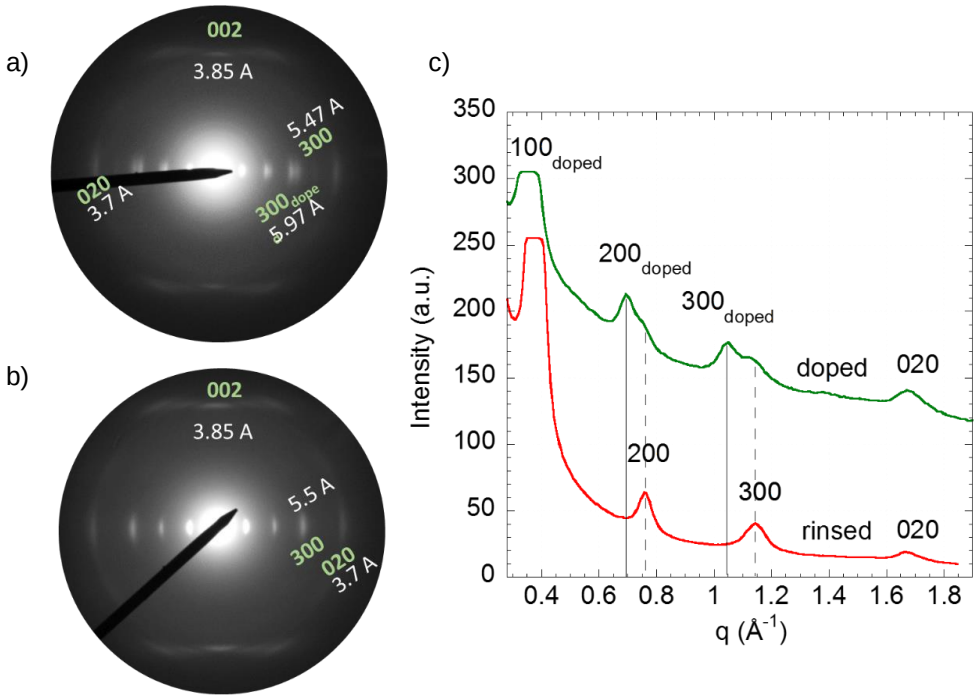

Figure S5. (a) Electron diffraction (ED) patterns of rubbed and Mo(tfdCOCF$_3$)$_3$-doped P3HT film before and (b) after rinsing the doped film with AcN. (c) Section profiles of ED patterns along the equator indicating doubling of the (*h*00) reflections due to the presence of two populations of crystallites (green curve); upon rinsing the ED pattern returns to the neat P3HT form (red curve).

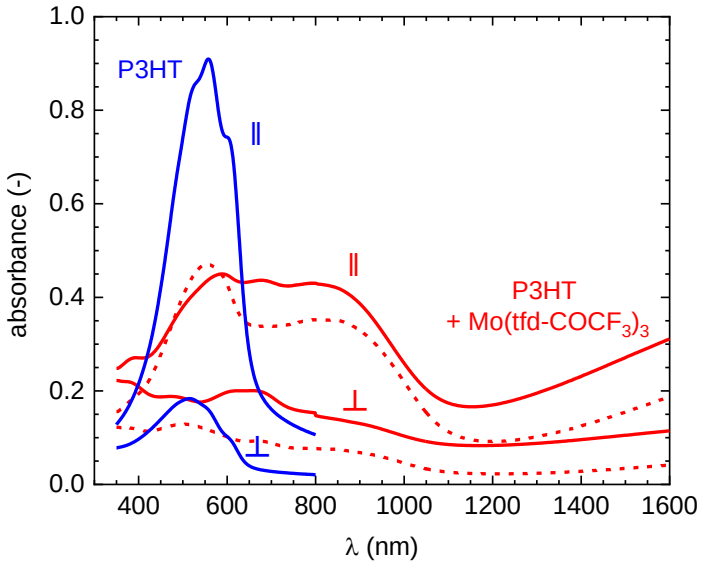

Figure S6. Polarized UV-vis-NIR absorbance spectra of rubbed P3HT (blue), rubbed P3HT doped with c_{Mo} ~ 2.5 g L^{-1} $Mo(tfd\text{-}COCF_3)_3$ (red solid line) and the same doped film after rinsing with AcN (red dashed line) measured parallel (∥) and perpendicular (⊥) to the rubbing direction; rinsing with AcN reduces the charge-carrier concentration from N_v ~ (3.6 ± 0.4)·10^{26} m^{-3} to (3.3 ± 0.4)·10^{26} m^{-3} and leads to an increase in the neutral polymer absorbance at 550 nm. Note the decrease in the vertical offset of the UV-vis-NIR spectra upon rinsing with AcN, which we explain with removal of excess dopant from the top of the film.

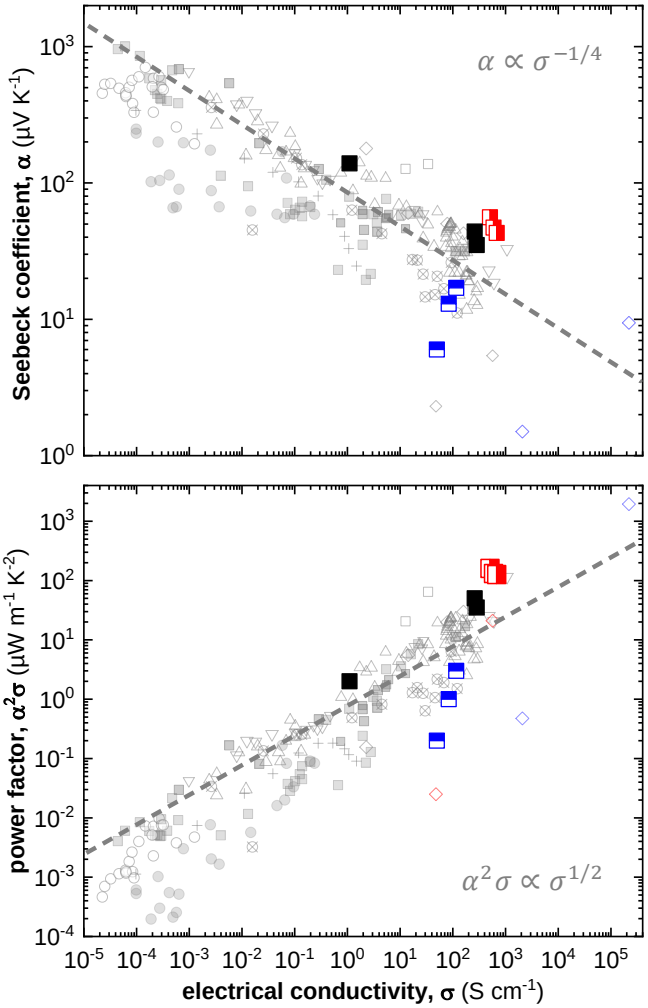

Figure S7. (a) Seebeck coefficient α and (b) power factor $\alpha^2\sigma$ versus electrical conductivity σ of isotropic P3HT (■), and rubbed P3HTmeasured parallel (◨) and perpendicular to the rubbing direction (⬒); grey data points are literature values extracted from ref. 1. as well as references therein; literature values are from ref. 2 (red and blue diamonds); dashed lines represent the empirical trends $\alpha \propto \sigma^{-0.25}$ and $\alpha^2\sigma \propto \sqrt{\sigma}$.

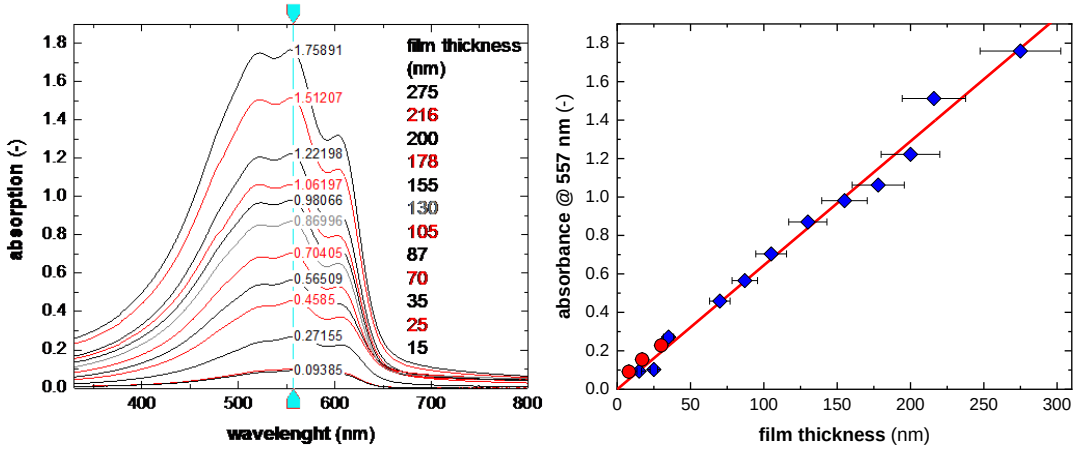

Figure S8. (a) Representative absorption spectra of spin-coated P3HT (M_n ~ 29 kg mol^{-1}, RR ~ 96 %, PDI ~ 2.2) from a 1:1 mixture of chlorobenzene:oDCB, the concentration of P3HT was varied from 2 to 30 g L^{-1} to obtain films with different thicknesses. The UV-vis absorption spectra were measured with a Pekin Elmer Lambda 950 spectrophotometer and the thickness was measured with a KLA Tencor AlphaStep D-100 profilometer. (b) Calibration curve for P3HT film thickness obtained by plotting the absorption at 557 nm versus film thickness. Average measurement deviation was ~ 5%, error bars in the graph represent an error of 10%. Blue diamonds: absorbance at 557 nm of spectra shown in Figure S8; Red circles: absorbance vs. thickness measured for films prepared with the P3HT batch used in this study (M_n ~ 24 kg mol^{-1}, RR ~ 95.9 %, PDI ~ 1.8).

1. Hynynen, J.; Kiefer, D.; Müller, C., Influence of crystallinity on the thermoelectric power factor of P3HT vapour-doped with F4TCNQ. *RSC Adv.* **2018,** *8*, 1593-1599.

2. Vijayakumar, V.; Zhong, Y.; Untilova, V.; Bahri, M.; Herrmann, L.; Biniek, L.; Leclerc, N.; Brinkmann, M., Bringing Conducting Polymers to High Order: Toward Conductivities beyond 10^5 S cm^{-1} and Thermoelectric Power Factors of 2 mW m^{-1} K^{-2}. *Adv. Energy Mater.* **2019,** *9*, 1900266.